SIMULATION OF REACTIVE DISTILLATION COLUMN FOR 2-ETHYL HEXYL ACRYLATE PRODUCTION FROM DILUTE ACRYLIC ACID

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ABSTRAK

Asid acrylate (AA) adalah asid organik yang tak tepu, bertoksik dan berbahaya terhadap alam sekitar. Malangnya, asid acrylate (AA) cair biasanya dihasilkan sebagai by-produk dalam pelbagai kimia dan petrokimia proses seperti pembuatan ester acrylate. Di kalangan penyelidik, pemulihan AA cair daripada aliran air sisa telah menjadi satu isu yang popular untuk dibincang oleh sebab isu-isu economic and alam sekitar. Pelbagai teknik pengasingan konvensional seperti penjerapan, penyulingan, dan pengekstrakan telah digunakan untuk merawat air sisa dari industri. Namun, teknik-teknik tersebut mempunyai kelemahan mereka masing-masing. Pemulihan AA melalui penyulingan reaktif telah menjadi salah satu kaedah yang menggalakkan dan ekonomi lestari untuk merawat air sisa. Setakat ini, kajian mengenai pengeteran AA cair melalui penyulingan reaktif tidak dilaporkan oleh penyelidik. Oleh itu, kajian simulasi terhadap pengesteran 2-ethylhexanol dengan AA cair melalui penyulingan reaktif akan disampaikan dalam kertas kerja ini. Kesan-kesan seperti kepekatan asid acrylate, nisbak refluks, kadar bawah, dan pemuatan pemangkin telah diubah serta konfigurasi optimum bagi penyuligan reaktif telah dikaji dalam karya ini. Keadaan operasi terbaik dan optimum konfigurasi bagi penyulingan reaktif seperti 10wt% kepekatan asid acrylate, 0.1 nisbah refluks, 0.13kg/h kadar bawah dan 1.5kg/m bebanan pemangkin telah dikenal pasti daripada keputusan simulasi. Konfigurasi penyulingan reaktif yang terbaik untuk system pengesteran AA cair dengan 2-ethylhexanol adalah lengkap dengan 18 peringkat terdiri daripada 4 tingkat reaktif, 10 tingkat pelucutan dan 4 tingkat pengayaan telah direka. Pemulihan maksimum asid acrylate dalam pengeteran AA cair dengan 2-ethylhexanol adalah 83%.

ABSTRACT

Acrylic acid (AA) is an unsaturated organic acid, very toxic and hazardous to the environment. Unfortunately, dilute acrylic acid (AA) has commonly produced as a by-product in many chemical and petrochemical processes such as manufacturing of acrylic esters. The recovery of dilute AA from the wastewater streams has become a growing concern among researchers due to its economic and environmental issues. There are several conventional separation techniques such as adsorption, distillation and extraction were developed to treat the wastewater from the industries; however, they have their own drawbacks respectively. One of the promising methods to purify the wastewater and economically sustainable is through esterification process of the recovery acrylic acid with alcohols via reactive distillation column. To date, study about esterification by using dilute AA has not been reported in literature. In this present work, a simulation study of esterification reaction of 2-ethylhexan-1-ol and dilute AA via reactive distillation system in the presence of ion exchange resin catalyst was performed using Aspen Plus RADFRAC incorporated with thermodynamic model of UNIFAC. The effect of different operating variables such as Acrylic Acid concentration, reflux ratio, bottom rate, catalyst weight and optimum column configuration were studied in this present work. The best operating conditions and column configuration were identified with maximum recovery of acrylic acid was 83% for the feed concentration of 10wt% AA, 0.1 reflux molar ratio, 0.13kg/h bottom rate and 1.5kg/m of catalyst weight. The best column configuration for the esterification system of acrylic acid and 2-ethylhexanol consisted of 4 reactive stages, 10 stripping stages and 4 rectifying stages, contributing to 18 numbers of stages with each stage of condenser and reboiler.

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1 INTRODUCTION

1.1 Background and Motivation of study

Acrylic acid and acrylate esters are widely used in the chemical industry. The market demand for these chemicals is nearly 4 MillionMT/yr, roughly split equally between acrylic acids and acrylate esters (Novemer, 2010). The production of these components has received increasing attention in Asia-Pacific region such as, China and South Korea due to the growing demands in super absorbent polymers in the market. Besides, great demand of acrylate ester such as 2-ethylhexyl acrylate in water-based coating and dispersion systems also has reached 2.8 millionMT in 2005 (NexantChem Systems, 2006). Thus, the demand trend for acrylic acid and its derivatives is forecast to increase gradually 4% per year in Asia-Pacific till 2018 (MarketsandMarkets, 2010). These have attracted many global companies such as BASF (Germany), Dow Chemical Company (U.S.), Nippon Shokubai (Japan), and others to venture into these markets.

2-ethylhexyl acrylate (2EHA) is one of the common acrylate ester which is commercially produced from 2-ethylhexan-1-ol (2EHOH) and acrylic acid (AA) by esterification process. It is colourless, volatile liquid, slightly soluble in water and completely soluble in alcohols and ethers and most organic solvents. It is used as a monomer in chemical industry for the production of homopolymers and copolymers (Komon *et al*., 2012). Both homopolymers and copolymers are mainly processed further to aqueous polymer dispersions. The aqueous polymer dispersions are used in adhesives, printing inks and binder for paints. They are also applied in the manufacturing of elastomers, super adsorbent polymers, flocculants, fibres and plastics.

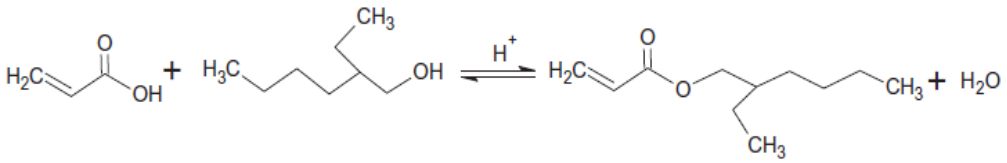
Acrylic acid, one of the reactant used to produce 2EHA is an unsaturated organic acid and is potentially a hazardous chemical to living species. It is released to the environment during the manufacturing of acrylic ester, water soluble resin and flocculants.In a typical acrylic manufacturing unit, the wastewater obtained from the quench tower containing high concentration of AA in the range of 4-10wt% along with several other toxicants of AA family such as acrylonitrile which is harmful to the environment (Kumar *et al*., 2010 Silva *et al*., 2003). The dissolved oxygen (DO) concentration of the receiving water stream polluted by the untreated wastewater can fall below the level necessary for normal aquatic organisms. Hence, removal of AA

from the wastewater is significantly important to protect the environment (Levec & Pintar, 2007).

Several treatment methods such as adsorption by activated carbon system (Kumar *et al*., 2010), wet air oxidation (WAO) (Silva *et al*., 2003), distillation and extraction (Arpornwichanop *et al*., 2008) are adopted to treat this type of wastewater. However, some of these methods are still suffering with the shortcomings of high operating cost and are inappropriate to treat the low concentration of wastewater with 4-15% of AA. Currently, wastewater from the industries is being treated using incineration process. Despite that, incineration is only suitable for highly concentrated wastewater at low flow rate (Kim & Ihm, 2011). On the other hand, recovery of AA from its dilute aqueous solution by using it as a reactant for esterification process could be a promising way (Singh *et al.*, 2006). The AA recovered from the wastewater can be used to produce a higher valued ester. This approach has brought much attention because it can save raw material cost and environmental problem.

1.2 Problem Statement

Esterification is a well-known chemical process that involves an acid and an alcohol to produce water and an ester as reaction product. To produce 2-ethyl hexyl acrylate, acrylic acid and 2-ethyl hexan-1-ol are esterified in a reversible equilibrium limited reaction shown in equation (1) (Komon *et al*., 2012):



AA EHOH EHA W (1)

Due to the reversible esterification reaction, the equilibrium of the esterification of the waste water containing AA with alcohol would be shifted away from the product. Excessive alcohol must be fed in to the reaction to shift the equilibrium to obtain ester as the reaction product. However, an excess alcohol feed have become the disadvantages due to the high cost separation process and recycled back after the reaction (Mueanmus *et al*., 2010). Currently, the production of 2-ethylhexyl acrylate (2EHA) is done by esterifying AA with 2-ethylhexanol (2EH) in conventional way by

using a continuous reactor followed by a series of separation units instead of using a RDC (Taylor & Krishna, 2000). Reactive distillation column (RDC) has become an attractive approach used to enhance an equilibrium limited esterification process in liquid phase (Buchaly et al., 2011) due to its special feature of insitu removal of product which can shift the equilibrium to the product side and yield the products, 2-ethyl hexyl acrylate. Figure 1 show (a) a typical conventional process consists of a reactor followed by a sequence of distillation columns. The mixture of A and B is fed into the reactor, where the reaction takes place in the presence of catalyst and reach equilibrium. A distillation train is required to produce pure products C and D. The unreacted components A and B will be recycled back to the reactor. (b) alternative reactive distillation column (RDC). The column consists of 3 sections of rectifying, reactive and stripping respectively. The rectifying section is at the top of the column followed by reactive section in the middle and lastly, the stripping section at the bottom of the column. The rectifying section is responsible to recover the reactant B from the product stream A while the stripping section is responsible to strip the reactant A from the product stream D.

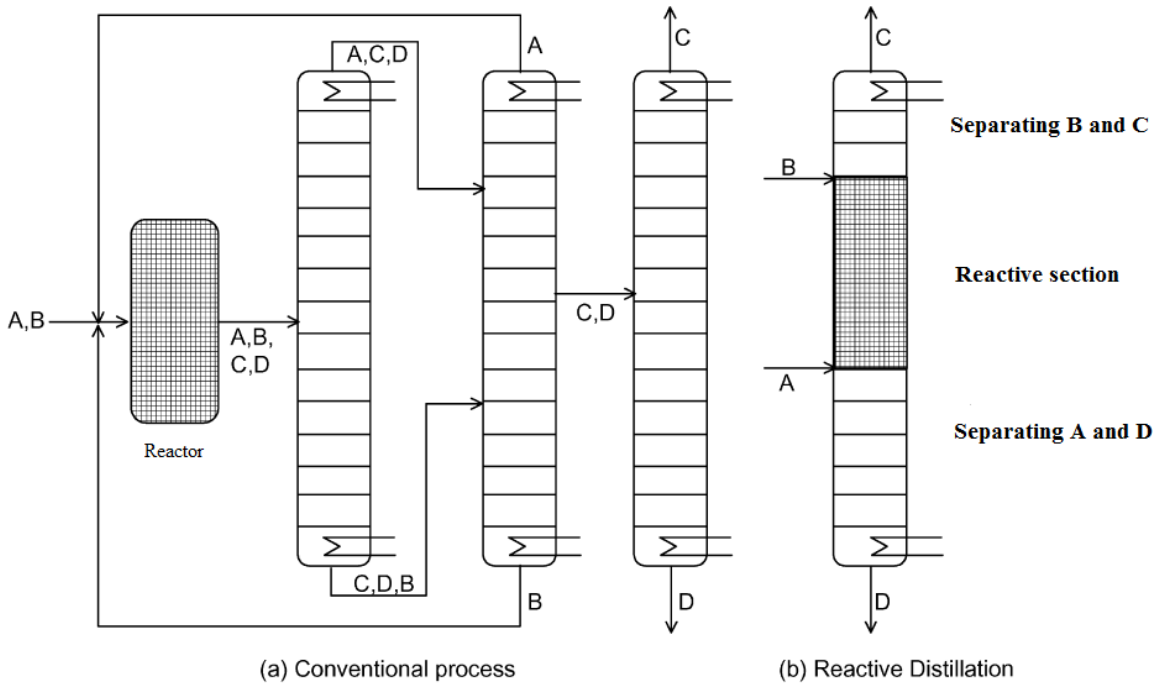


Figure 1. 1: Processing schemes for a reaction sequence $A+B \leftrightarrow C+D$ where C and D are both desired products. (a) Typical configuration of a conventional process consisting of a reactor followed by a series of distillation column. (b) The configuration of a

reactive distillation column. The components A, C, D and B have increasing boiling point (Taylor & Krishna 2000).

It is expected that esterification of waste water containing AA with 2-ehyl hexa-1-ol (2EHOH) in a RDC would be a promising method to recover AA. To the best of our knowledge, open literature about synthesis of 2-ethyl hexyl acrylate (2EHA) by reacting diluted acrylic acid with 2-ethyl hexan-1-ol (2EHOH) in a RDC is limited. Therefore, the present study focuses on the simulation study of the RDC for the production of 2EHA from the diluted AA and 2EHOH. The feasibility and practicability of AA recovery from the diluted aqueous solution using RDC are examined.

1.3 Objectives

The objectives of the present study include:

- To examine the efficiency of AA recovery from the diluted aqueous solution using RDC
- To investigate the effect of different important operating parameters for the reactive distillation column (RDC).

1.4 Scope of Study

In the present research, an intensive simulation study of the esterification of acrylic acid with 2-ethyl haxan-1-ol heterogeneously catalysed by acidic ion-exhange is performed using Aspen Plus version 7.0. Equilibrium model (RADFRAC) is chosen to simulate the RDC with the incorporation of suitable thermodynamic properties and reaction kinetics.

The verification is first done on esterification of acrylic acid and other alcohols from the past researchers to check the accuracy of the model. After obtaining validated model, it is adopted for the simulation study for esterification of acrylic acid and 2-ethylhexanol via RDC. Then, the practicability of the reaction is examined through the acrylic acid conversion in the RDC.

In this study, several operating parameters such as concentration of AA in the feed, reflux ratio, bottom rate, and catalyst weight are varied during the simulation studies. The ranges of these parameters are concentration of AA (10wt%-30wt %),

reflux molar ratio (0.1-0.2), bottom rate (0.01-0.13 kg/h), and catalyst weight (0.5-2.0 kg/m). The best operating condition to maximize the AA recovery is identified. Besides that, the column configuration for RDC is determined in this present paper work.

1.5 Organisation of this Partial Thesis

This partial thesis is divided into four chapters. Chapter 1 (introduction) presents a brief description about the demands of acrylic acids and acrylate esters in Asia-Pacific. The harmful of wastewater discharged containing acrylic acid to the environment and the conventional processes used to treat this wastewater is also briefly discussed. This chapter includes the problem statement that provides some guidelines for identifying the research directions and objectives. The objectives and scopes of study are then elucidated in detail. Finally, the organization of the partial thesis is given.

Chapter 2 (Literature review) provides information the shortcoming of the conventional method used to purify the wastewater, recovery of carboxylic acid through esterification reaction and application of RDC in esterification system are discussed, and several important considerations such as catalysts, kinetics thermodynamics and modelling for the RDC implementation are surveyed.

The simulation procedures are illustrated in detail in chapter 3 (Methodology). In this chapter, an appropriate RD model is chosen to simulate the RDC by incorporating the suitable thermodynamic properties and reaction kinetics of the esterification system. A step-by-step guide for the simulation study is also included.

Chapter 4 discusses the results obtained from the simulation. The accuracy of the model is discussed based on the model validation results. performed to check the. The validated model is then applied for the simulation of the esterification of acrylic acid and 2-ethyl hexan-1-ol under different operating parameters such as concentration of acrylic acid (10-30wt%), reflux ratio (0.1-0.2), bottom rate (0.01-0.12 kg/h), and catalyst weight (0.5-2.0 kg/m). The results are deliberated to identify the most significant effect, the best operating parameter and column configuration that yield highest conversion.

Chapter 5 summarises the thesis for the simulation studies and suggestions are outlined to develop in future work.

2 LITERATURE REVIEW

2.1 Overview

This chapter presents the literature review from past researchers about the problem of acrylic acid discharged into the water stream; types of wastewater treatment method; recovery of carboxylic acid via esterification system; reactive distillation technology; application of RDC in esterification system; catalyst in esterification system and modelling of reactive distillation.

2.2 Introduction

Various types of wastewater containing toxic and hazardous organic compounds are generated by the chemical and petrochemical industries. Acrylic acid is one of the hazardous organic acids that presents in this industrial wastewater. It brings harmful effects to the living species such as irritation to the skin, eyes and respiratory system. In a typical AA manufacturing plant, the wastewater containing concentration of AA in the range of 10-20% is being produced (Kumar *et al*., 2010). The discharge of this waste water would create a lot of complications to the environment due to high toxicity of organic compound. The level of dissolved oxygen (DO) concentration of the water streams should be below the level that necessary for the aquatic life to survive (Lin *et al*., 1996).The waste elimination matter has gained a lot of concerns from the researchers (Debellefontaine & Foussard, 2000). The industrial wastewaters must be treated to a level which is safe to be disposed to the natural water streams (Levec & Pintar, 2007).

2.3 Type of Industrial Wastewater Treatments

Several conventional separation techniques such as activated sludge treatment (Lin *et al*., 1996), distillation and extraction (Arpornwichanop *et al*., 2008) are adopted to treat the wastewater containing acrylic acid from the industries. Adsorption and wet air oxidation are the treatment methods under research (Kumar *et al*., 2010; Silva *et al*., 2003).

Activated sludge treatment is a type of traditional biological method used to recover AA from wastewater. The activated sludge system is not a complex treatment

and this eventually makes it relatively low cost to operate (Lin *et al.*, 1996). However, the microorganism in the activated sludge system requires a long residence time to degrade the pollutants. Thus, the biological sludge system can only deal with relatively low concentration of organic compounds. Moreover, this treatment is not suitable to treat the toxic contaminants due to biomass poisoning (Kim & Ihm, 2011). The conventional distillation is also used to purify the wastewater; however it is highly uneconomical because of large amount of water is required to vaporize from dilute aqueous solution due to the high latent heat of vaporization of water which makes it impractical (Gangadwala *et al*., 2008). Acoording to Ashton (2013), the conventional distillation managed to recover low concentration of acetic acid from wastewater, which in the range of 0.4-0.8wt%. Besides, the extraction also suffers from several drawbacks such as the separation process is limited by phase separation and distribution of components involved in the reacting system (Bianchi *et al.*, 2003). This method is used to recover AA from wastewater in the range of 7-12wt% (Shin *et al*., 2008).

Kumar *et al*. (2010) have used powdered activated carbon (PAC) as an adsorbent in their research work to remove AA from wastewater. They have found that adsorption treatment for recovery of AA from wastewater to be efficient and relatively low cost. Aluminium, alumina, titanium dioxide and clay minerals are a few examples of the adsorbent for the treatment used in laboratory scale adsorption experiment. Despite that, adsorption approach can only be used to treat low concentration of organic compounds present in wastewater.

Due to development of innovative technology, wet air oxidation (WAO) separation technique has been adopted to treat the wastewater and substituted the adsorption and activated sludge methods. The main reason WAO has replaced adsorption method is because it can remove high concentration of organic compounds in chemical wastewaters (Li *et al*., 1991). The WAO processes have the ability to break the organic compounds to simpler, easily treated materials before they are released into the environment. In general, it has a very limited interaction with the environment, which makes it environmental friendly (Levec & Pintar, 2007). Typical operating conditions were needed for WAO processes: high temperature at 200- 325˚C and high pressure at 50-175 bar to partially oxidize the organic pollutants into biodegradable intermediates to carbon dioxide, water and innocuous end products (Kim *et al.*, 2011).

Unfortunately, the severe operating condition of WAO has caused high capital cost and energy consuming (Oliviero *et al.*, 2001).

Recovery of AA by esterification process with the aid of reactive distillation could be one of the most promising and interesting treatment method used to purify industrial wastewater. Ragaini *et al*. (2006) have reacted the dilute acetic acid (4.5-15%wt) with alcohol in the presence of catalyst to produce ester. The main advantage to treat the wastewater by using esterification is that it can produce a good value of ester on top of reducing the environmental problem.

2.4 Recovery of Carboxylic Acid via Esterification Reaction

Acetic acid has been successfully recovered from dilute aqueous solutions through esterification with methanol by using RDC (Singh *et al.*, 2006). Besides that, other acids such as lactic acid, adipic acid, mystiric acid, succinic acid, chloroacetic acid, glycolic acid and trifluroacetic acid can also be recovered from their dilute solution with RDC (Yogesh & Singh, 2008).

The recovery of acetic acid (30% wt) with methanol by reactive distillation in the presence of ion exchange resin catalyst has been investigated by Singh *et al*. (2006) for both the simulation and experimental studies. A pseudohomogeneous kinetic model was used during the simulation. The studies on the effect of the operating parameters such as reboiler duty, feed flow rate and feed composition also have been covered in the simulation study. The results showed a quantitative recovery as high as 80% of acetic acid for the feed concentration of 30%wt in a laboratory column. Besides that, the researchers have also proposed three feasible alternative of configuration to complete recover the acid in the system.

Similarly, Saha *et al*. (2000) have also studied the effect of operating variables, such as, feed flow rate, feed location, reflux ratio, molar ratio of reactant and the effect of recycle of water on the recovery of 30% acetic acid by reacting with n-butanol and iso-amyl alcohol respectively in a RDC using ion-exchange resin, Indion 130 cation exchange resin, as a catalyst. The results showed that at 1:2 molar ratio of acetic acid to butanol, approximately 58% conversion of acetic acid was realized; while at 1:2 molar ratio of acetic acid to iso-amyl, almost closely of 51% conversion of acetic acid was

achieved. The best result was obtained when the column was operated in counter current mode.

Bianchi *et al*. (2003) have presented the recovery of a diluted acetic acid (6wt %) by reacting with n-butanol and 2-ethylhexanol in a simple glass reactor. The peculiarity of this method is the presence of large amount of water at the beginning of the reaction. The esterification reaction in the glass reactor is thermodynamically favourable as it has the ability to shift the reaction equilibrium towards the ester and not towards the reagent.

The feasibility of recovery of trifluroacetic acid (TFA) from dilute aqueous solution by reactive distillation has been studied by Yogesh and Singh (2008). The experimental investigation was carried out by reacting the recover TFA with 2-propanol via RD in batch and continuous modes. The experiments result show an increased conversion of TFA and it is confirmed that through simulation with either incorporated equilibrium stage model or non-equilibrium stage model, the recovery system can yield greater than 97% recovery.

2.5 Reactive Distillation Technology and Applications

The concept of reactive distillation for esterification process has been introduced by Backhaus starting in 1921. Despite the fact that the basic concept of combining reaction and distillation is old, there has been an enormously growing interest in the design and operation of RD process in recent year. In RD column, the chemical reaction and separation by distillation occurs simultaneously in one unit operation (Niesbach *et al*., 2012). A RDC consists of a reaction section in the middle with non-reactive rectifying and stripping sections at the top and bottom respectively. The task of rectifying section is to recover reactant B from the product C. In the stripping section, the reactant A is stripped from the product stream D. In the reactive section, the products are separated in situ, driving the equilibrium to the right and preventing any undesired side reaction between the reactants A (or B) with the product C (or D). The components A, C, D, and B have increasing boiling points. The general configuration of RDC is shown in figure 2.1 (Shinde *et al*., 2011).

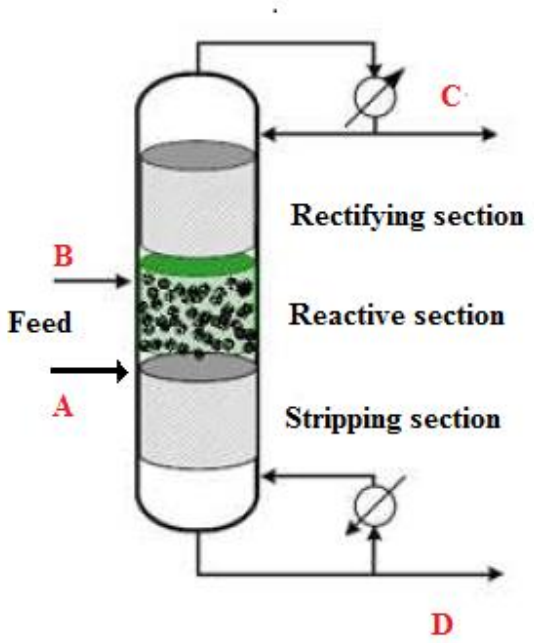


Figure 2. 1: The general configuration of Reactive Distillation (RD).

The development of innovative reactive distillation based on ecologic and economic aspects has evolved into a promising process alternative to conventional sequential processes especially for equilibrium limited and consecutive reactions (Steinigeweg & Gmehling, 2002). RD is successfully implemented in several reactions, for examples, etherification, esterification, alkylation, hydrogenation, hydration and hydrolysis that incorporated with solid heterogeneous catalyst, in another term RD is also called as catalytic distillation process (Murat *et al*., 2003).

Reactive distillation (RD) has many distinctive advantages and it is summarized as follows (Taylor & Krishna, 2000; Murat *et al.*, 2003; Tuchlenski *et al.*, 2001):

- Reduction in capital investment. This is because the two process steps can be carried out in the same unit operation. Besides that, the amount of equipment such as pump, piping and instrumentation also can be reduced significantly.
- Increased conversion of reactants. The in-situ removal of products from the reactive zone has pushed the chemical equilibrium to the forward direction based on Le Chatelier's Principle. The forwarded chemical equilibrium in the reaction has results a significant yield of products.

- Improved products selectivity. The products selectivity can be improved due to fast removal of reactants or products from the reactive zones. The maintaining low concentration of one the reagents can lead to reduction of the rates of side reactions and thus improved the selectivity of the desired products.
- Lower energy consumption. If esterification is an exothermic reaction, the heat of reaction can be used for vaporisation of liquid and hence, the reduction of reboiler duties can cause the energy consumption to be lowered.
- Avoidance of azeotrope. RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes to be "reacted away" in a single vessel.
- Environmental friendly

Besides the above-mentioned advantages of RD, there are several constrains and difficulties for implementing RD technology.

- Volatility constraints. Appropriate volatility of reagents and products is a must to maintain the high concentrations of reactants and low concentrations of products in the reactive zone.
- Residence time requirement. The residence time for the reaction is long in the reactive zone requires a large column size with large tray hold-ups. This may cause RD to be more non-economic than the conventional reactor-separator arrangement
- Scale up to large flows. It is difficult to design RD processes for very large flow rates because of liquid distribution problems in packed RD columns.
- Process conditions mismatch. In some processes the optimum conditions of temperature and pressure for distillation may be far from the optimum reaction and vice versa.
- Liquid phase conditions. Wet catalysts pellets are necessary if the chemical reaction is take place in liquid phase.

- Long lifetime of catalyst needed. As it is very expensive to change the catalyst in the structured catalytic packing in RDC. A long lifetime of catalysts is strongly required.

Esterification is a well-known chemical process that involves two reactants; an alcohol and an acid in the presence of acid catalyst which produce an ester as reaction product. This process has attracted a lot of researchers' attention to make it as a subject for extensive investigation (Syed Azhar *et al*., n.d.).

Steinigeweg and Gmehling (2002) have presented a study of the development of heterogeneously catalysed RD process for the production of n-butyl acetate using the reliable thermodynamic and kinetic data. The reaction was catalysed by strongly acidic ion-exchange (Amberlyst 15). The experimental results were compared with the simulation results which indicate that an equilibrium stage model is able to describe the experiments quantitatively. On the other hand, the influence of design factors such as feed location, use of prereactor, number of reactive and nonreactive stages were determined by the help of simulation study. The same conclusion was shown from the study of feasibility of RDC for producing n-butyl acetate using different heterogeneous catalyst; for example, surface-sulfonated ion-exchange resin Amberlyst 46 (Hui *et al*., 2012). From the simulation results, n-butanol conversion and n-butyl acetate purity have reached greater than 96% at the optimal conditions.

The esterification of acetic acid with ethanol has been widely investigated by researchers, mainly because it is an important organic solvent used in the chemical industry (Lai *et al*., 2008). Both Kirbaslar *et al*. (2000) and Calvar *et al*. (2007) have studied the reaction kinetics of the esterification process of ethanol with acetic acid which catalysed by heterogeneous and homogeneous catalysts at the temperature range of 303.15˚C to 353.15˚C. Besides that, they have also done several investigations on the effect of the operation parameters such as reflux ratio, feed flow rate and vapor rate on the production of ethyl acetate. Kirbashlar *et al*. (2000) showed the results of highest ethyl acetate composition is obtained when the packed bed reactive column operated in continuous mode; while Calvar *et al*. (2007) showed that the purity of ethyl acetate in distillate is limited by the azeotropic composition. As for Lai *et al*. (2008), production of high purity of ethyl acetate has been researched experimentally. A product of more than 99% of ethyl acetate and less than 100ppm of acetic acid is expected to achieve as

the specification. The results of six experiment run show that with the proper design of reactive distillation, a highly purity of ethyl acetate will be obtained.

As a summary, the application of RDC in esterification systems is acknowledged by a lot of past researchers because it can produced a good value of esters as final product at optimum operating conditions. The application of RDC in esterification systems have been summarized in the Table 2.1.

Table 2. 1: The application of RDC for the esterification systems.

Esterification system	**Type of catalyst**	**References**
$n-Butanol + Acrylic\ \ acid \rightarrow n-Butylacrylate + Water$	Amberlyst 15	Niesbach *et al.*, 2012
$n-Butanol + Acetic\ \ acid \rightarrow n-Butylacetate + Water$	Amberlyst 36 Wet	Hui *et al.*, 2012
	Amberlyst 15	Steinigeweg & Gmehling, 2002
$Ethanol + Acetic\ \ acid \rightarrow Ethylacetate + Water$	Amberlyst 15	Kirbashlar *et al.*, 2000
	Acetic acid (homogeneous); Amberlyst 15 (heterogeneous)	Calvar *et al.*, 2007
	No information	Kenig *et al.*, 2001
	Amberlyst 36 Wet	Lai *et al.*, 2008
$1-Propanol + Propionic\ \ acid \rightarrow n-Prorylpropionte + Water$	Amberlyst 46	Buchaly *et al.*,

		2012
$n-Hexanol + Acetic\ \ acid \rightarrow Hexylacetate + Water$	Amberlyst CSP2	Schmitt *et al.*, 2004
$Methanol + Decanoic\ \ acid \rightarrow Decanoate + Water$	Amberlyst 15	Steinigeweg & Gmehling, 2003

2.6 Catalysts in Esterification System

Catalysts were added into the liquid phase esterification in order to speed up the rate of reaction and increase the conversion of the reactants (Ahmed Zeki *et al*., 2010). The kinetic model and reaction mechanism for carboxylic acids esterification over homogeneous acids and heterogeneous catalysts have been well documented in the literature (Miao & Shanks, 2011).

The mechanism for homogeneous catalysis in esterification reaction involves protonation of carboxylic acid, which activates it for the reaction with the nonprotonated alcohol to yield a tetrahedral intermediate that, by decomposition. This will result in the production of ester and water. The slow step of the reaction is the nucleophilic attack of the alcohol on the protonated carbonyl group of the carboxylic acid (Liu *et al.,* 2006).

Two mechanisms have been proposed for esterification on heterogeneous acid catalysts: a single-site mechanism (Eley-Riedel, E-R) and a dual site mechanism (Langmuir-Hinshelwood type, L-H) (Miao & Shanks, 2011). The schematic diagram for the heterogeneous catalysis reaction mechanism is shown in Figure 2.2. In heterogeneous catalysis reaction, there are seven steps involved in the reaction mechanism. Steps 1 and 2 show the diffusion of the reactant form the bulk fluid into the external and internal surface of the catalyst pellet respectively. Similarly for steps 6 and 7, it shows the diffusion of reactant out from the external and internal surface of the catalyst pellet back into the bulk fluid respectively. Step 3 shows the adsorption of the

reactant A onto the catalyst surface continue by step 4 shows the reaction on the surface of the catalyst and lastly step 5 which is desorption of the product from the catalyst surface (Fogler, 1999).

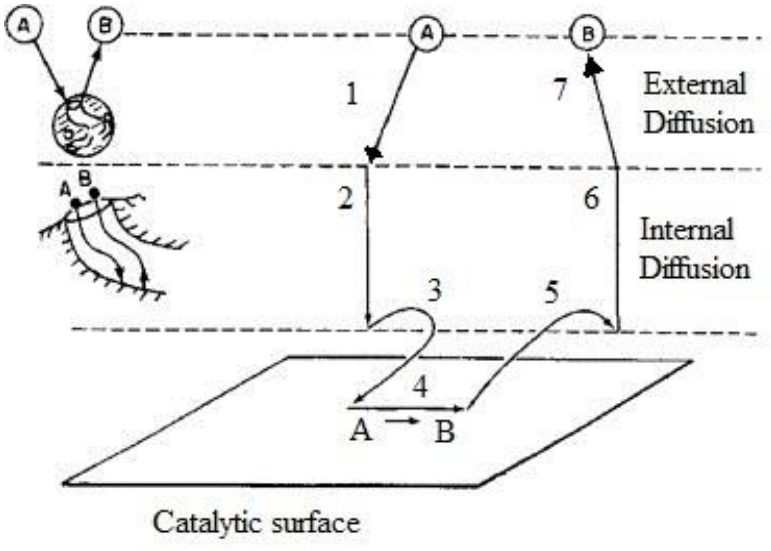


Figure 2. 2: The heterogeneous catalysis reaction mechanism

2.6.1 Homogeneous Catalyst

In esterification reaction, strong mineral liquid acids, such as sulphuric acid and p-toluenesulphonic acid are widely applied in the reaction. The catalytic activity of homogeneous catalysts is extremely high (Peters *et al.,* 2006). Despite a strong catalytic effect, the use of homogeneous catalyst, for example sulphuric acid has posed several drawbacks which include the generation of large amount of toxic wastewater, equipment corrosion and loss of catalyst (Yogesh & Singh, 2011; Chen *et al*., 1999).

Production of n-propyl acetate by reactive distillation which catalysed with homogeneous acidic catalyst, sulphuric acid was carried out experimentally by Brehelin *et al.* (2007). The results from the experiment showed that the acetic acid conversion has reached 79% with molar purity of n-propyl acetate of 64% have been achieved. Besides that, the researchers have done a simulation study for the optimum design of reactive distillation to obtained optimum production. The simulation results have shown a good agreement with experimental data.

Synthesis of acetic esters, including methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate using *p*-toluene sulphonic acid (PTSA) with sulfuric group as homogeneous catalyst was studied by Yao *et al.* (2009) in a microchanels reactors.

The highest yields of esters happened when the reaction temperature was near to the lowest boiling point of the components. The experimental results showed that the yields reached 74.0, 70.1, 97.2, and 92.2% for methyl acetate, ethyl acetate, n-propyl acetate n-butyl acetate production respectively.

The esterification kinetics of acetic acid with ethanol in the presence of sulfuric acid as homogeneous catalyst was studied by Ahmad Zeki *et al*. (2010). The investigation was carried out experimentally with isothermal batch at temperature of 50-60˚C. It was found that the rate constant and conversion at a certain mole ratio increased when the temperature of the reaction increased. From the results, it is found that the maximum conversion, approximately 80% as obtained at 60˚C for molar ratio of 10:1 ethanol to acetic acid.

2.6.2 Heterogeneous Catalyst

Zeolites, heteropolyacids, sulfated, metal oxides and ion exchange resin such as Amberlyst are some of the examples of solid acid catalyst used in many chemical industries (Shanmugan *et al*., 2004). According to Toor *et al*. (2011), ion exchange organic resin such as Amberlyst 35, Amberlyst 36, and Dowex 50W are the most popular solid catalyst used to produce esters. It is found that ion-exchange resins offer better selectivity toward the desired products compared to homogeneous. The drive to develop green processes has led to the development of solid acid catalysts to a significant increase in research studies both in academic and industrial section. These materials can substitute the corrosive liquid acids which are used in the industry in the olden days. Heterogeneous catalysts offer a few distinct advantages over catalysis by homogeneous catalysts (Teo & Saha, 2004):

- Environmental friendly due to corrosive environment eliminated.
- The purity of the products is higher as the side reactions can be completely eliminated or significantly less.
- Easy removal of catalyst from the reaction mixture by filtration.

In order to maintain the economic viability, suitable heterogeneous system must not only minimize the production of waste but should also exhibit high activities and selectivities comparable to the existing homogeneous route (Wilson & Clack, 2000).